11 The particle in a three-dimensional box

11.1 The Schrödinger equation in three dimensions

How do we generalize the Schrödinger equation to more than one dimension, say in three dimensions? A point in three dimensions is specified by a vector $\mathbf{r} = (x, y, z)$. Wave functions for particles that move in three dimensions will then have to depend on all of these three variables

$$\psi(x) \to \psi(x, y, z). \tag{1}$$

The wave function $\psi(x, y, z)$ is now a complex function that depends on multiple variables. As we will see, this introduces several complications that will require some advanced mathematical techniques.

Operators for a particle in three dimensions will also become vectors. For example, the position operator $\hat{x}$ becomes

$$\hat{x} \to \hat{\mathbf{r}} = (\hat{x}, \hat{y}, \hat{z}), \tag{2}$$

where $\hat{x}$, $\hat{y}$, and $\hat{z}$ are position operators for the x, y, and z axes, respectively. Similarly, the momentum operator will become a vector

$$\hat{p} \to \hat{\mathbf{p}} = (\hat{p}_x, \hat{p}_y, \hat{p}_z) = \left(-i\hbar\frac{\partial}{\partial x}, -i\hbar\frac{\partial}{\partial y}, -i\hbar\frac{\partial}{\partial z} \right). \tag{3}$$

When we write the kinetic energy operator in three dimensions we have to keep into account that it comes from the square of the momentum operator vector

$$\hat{T} = \frac{\hat{\mathbf{p}}^2}{2m} = \frac{\hat{\mathbf{p}} \cdot \hat{\mathbf{p}}}{2m} = \frac{\hat{p}_x^2 + \hat{p}_y^2 + \hat{p}_z^2}{2m} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) = -\frac{\hbar^2}{2m}\nabla^2. \tag{4}$$

Here we have expanded the square of the momentum operator as we would do with any vector by summing the square of each component. In the last term we have written the kinetic operator using the Laplacian operator.[1]

The total Hamiltonian in three dimension is the sum of the kinetic operator plus a potential operator that depends on all thee coordinates ($\hat{V}(x, y, z)$)

$$\hat{H} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) + \hat{V}(x, y, z). \tag{5}$$

[1] The Laplacian is the sum of partial second derivatives, $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$. In other words, the Laplacian is the divergence ($\nabla\cdot$) of the gradient ∇, that is $\nabla^2 = \nabla \cdot \nabla$.

11.2 A theorem on separable Hamiltonians

How can we deal with the Hamiltonian in three dimensions? Here we will take a look at a method that allows us to simplify the solution of problems in more than one dimension when the Hamiltonian is **separable**. Consider the simpler case of a particle in two dimensions (x, y) and suppose that the Hamiltonian is separable into two Hamiltonians that depend on only one of these two variables

$$\hat{H} = \hat{H}_x + \hat{H}_y. \tag{6}$$

In this case, if we know how to solve the Schrödinger equation for each individual Hamiltonian $\hat{H}_x$ and $\hat{H}_y$, then we can easily find the solutions to the full Hamiltonian $\hat{H}$. Suppose that we know the eigenvalues/eigenfunctions of $\hat{H}_x$ and $\hat{H}_y$

$$\hat{H}_x\psi_x(x) = E_x\psi_x(x), \tag{7}$$

$$\hat{H}_y\psi_y(y) = E_y\psi_y(y), \tag{8}$$

then the eigenvalue (E) and eigenfunction [$\psi(x,y)$] of the full Hamiltonian $\hat{H}$ are given by

$$E = E_x + E_y, \tag{9}$$
$$\psi(x,y) = \psi_x(x)\psi_y(y). \tag{10}$$

To see that $\psi(x,y) = \psi_x(x)\psi_y(y)$ is an eigenfunction of the full Hamiltonian we plug it in the Schrödinger equation

$$\begin{aligned}
\hat{H}\psi(x,y) =& \hat{H}\psi_x(x)\psi_y(y) \\
=& (\hat{H}_x + \hat{H}_y)\psi_x(x)\psi_y(y) \\
=& \hat{H}_x\psi_x(x) \underbrace{\psi_y(y)}_{\text{independent of } x} + \hat{H}_y\psi_x(x)\psi_y(y) \\
=& \psi_y(y)\underbrace{\hat{H}_x\psi_x(x)}_{E_x\psi_x(x)} + \psi_x(x)\hat{H}_y\psi_y(y) \\
=& E_x\psi_y(y)\psi_x(x) + E_y\psi_x(x)\psi_y(y) \\
=& (E_x + E_y)\psi_x(x)\psi_y(y) = (E_x + E_y)\psi(x,y).
\end{aligned} \tag{11}$$

In the end we find out that $\psi(x,y) = \psi_x(x)\psi_y(y)$ is indeed an eigenfunction of the Hamiltonian and that the corresponding eigenvalue is $E_x + E_y$.

11.3 The particle in a three-dimensional box

Now we are ready to study the case of a particle in a three-dimensional box. We will assume that the box is rectangular and has edge lengths equal to L_x, L_y, and L_z. In this case, the potential operator is given by

$$\hat{V}(x,y,z) = \begin{cases} 0 & \text{if} \quad 0 \le x \le L_x, 0 \le y \le L_y, 0 \le z \le L_z \\ \infty & \text{otherwise.} \end{cases} \tag{12}$$

The wave function also has to satisfy the following condition

$$\psi(x,y,z) = 0 \quad \text{for } (x,y,z) \text{ outside the box,} \tag{13}$$

and by demanding that the wave function is continuous we obtain the boundary condition

$$\psi(x,y,z) = 0 \quad \text{for } (x,y,z) \text{ on the borders of the box.} \tag{14}$$

When can then focus only on what happens inside the box and write the Hamiltonian

$$\hat{H} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) = \hat{T}_x + \hat{T}_y + \hat{T}_z, \tag{15}$$

where $\hat{T}_x$ is the kinetic energy operator for a particle in the x dimension. Note that this Hamiltonian separates into three independent terms, $\hat{T}_x$, $\hat{T}_y$, and $\hat{T}_z$, of which we know eigenvalues and eigenfunctions. In the case of the x coordinate we have the eigenfunctions [$\psi_{n_x}(x)$] and eigenvalues (E_{n_x})

$$\begin{aligned}
\psi_{n_x}(x) &= \sqrt{\frac{L_x}{2}} \sin\left(\frac{n_x \pi x}{L_x}\right) \\
E_{n_x} &= \frac{h^2 n_x^2}{8mL_x^2},
\end{aligned} \tag{16}$$

where $n_x = 1, 2, \ldots$ is the particle in a box quantum number for the x dimension. Similar equations can be written for the y and z components of the Hamiltonian.

If we apply the theorem on separable Hamiltonians we get that the total wave function is the product of solutions for the x, y, and z directions

$$\begin{aligned}\psi_{n_x,n_y,n_z}(x,y,z) =& \psi_{n_x}(x)\psi_{n_y}(y)\psi_{n_z}(z) \\ =& \sqrt{\frac{8}{L_xL_yL_z}} \sin\left(\frac{n_x\pi x}{L_x}\right) \sin\left(\frac{n_y\pi y}{L_y}\right) \sin\left(\frac{n_z\pi z}{L_z}\right),\end{aligned} \tag{17}$$

while the total energy is given by

$$E_{n_x,n_y,n_z} = E_{n_x} + E_{n_y} + E_{n_z} = \frac{h^2}{8m}\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right). \tag{18}$$

11.4 Energy levels of a cubic box and degeneracy

For a cubic box

$$L_x = L_y = L_z = L \tag{19}$$

and the energy expression simplifies to

$$E_{n_x,n_y,n_z} = \frac{h^2}{8mL^2}(n_x^2 + n_y^2 + n_z^2) = E_1(n_x^2 + n_y^2 + n_z^2), \tag{20}$$

where E_1 is the **energy of the lowest state of the particle in a 1D box** of length L.

The lowest energy level for the particle in a 3D cube is

$$E_{1,1,1} = \frac{h^2}{8mL^2}(1^2 + 1^2 + 1^2) = 3E_1. \tag{21}$$

The next level is

$$E_{2,1,1} = E_1(2^2 + 1^2 + 1^2) = 6E_1. \tag{22}$$

Note that this state is degenerate with two other states since

$$E_{2,1,1} = E_{1,2,1} = E_{1,1,2} = 6E_1. \tag{23}$$

We say that the level $6E_1$ is triply degenerate. These states have the same energy but their wave functions are different. This can be easily seen by comparing them. For example,

$$\psi_{2,1,1}(x,y,z) = \psi_2(x)\psi_1(y)\psi_1(z), \tag{24}$$

while

$$\psi_{1,2,1}(x,y,z) = \psi_1(x)\psi_2(y)\psi_1(z). \tag{25}$$

These two wave functions are distinct and are not related via a phase factor. However, note that if we perform the following coordinate transformation

$$x \to y, \quad y \to x, \quad z \to z, \tag{26}$$

on the function $\psi_{1,2,1}(x,y,z)$ we obtain

$$\psi_{1,2,1}(y,x,z) = \psi_2(x)\psi_1(y)\psi_1(z) = \psi_{2,1,1}(x,y,z). \tag{27}$$

So, the two functions are related by a geometry transformation, in this case a rotation around the z axis. This point illustrates the fact that the degeneracy of these states arises from the symmetry of the problem that we are trying to solve. The cube can be rotated in several ways, and all these transformations leave the potential unchanged. As a consequence, some states are degenerate and their wave functions are related via a geometric transformation.

The particle in a 3D box also has states with degeneracy equal to six. Consider the state

$$E_{3,2,1} = E_1(3^2 + 2^2 + 1^2) = 14E_1. \tag{28}$$

There are six permutations of the numbers $1, 2, 3$, and this means that there are six different states with energy equal to $14E_1$

$$E_{3,2,1} = E_{3,1,2} = E_{2,1,3} = E_{2,3,1} = E_{1,2,3} = E_{1,3,2} = 14E_1. \tag{29}$$

Note that some levels are **accidentally degenerate**. For example, the levels $E_{3,3,3}$ and $E_{5,1,1}$ have the same energy:

$$E_{3,3,3} = E_1(3^2 + 3^2 + 3^2) = 27E_1, \tag{30}$$

$$E_{5,1,1} = E_1(5^2 + 1^2 + 1^2) = 27E_1. \tag{31}$$

In this case we talk about degeneracy being accidental because the corresponding wave functions $\psi_{3,3,3}$ and $\psi_{5,1,1}$ cannot be transformed into each other by a symmetry operation (rotation, reflection, inversion).

11.5 Expectation value

To evaluate expectation values for a particle in a box we just need to generalize the definition given previously. For a generic wave function $\psi(x, y, z)$ and an operator $\hat{A}$, the expectation value of $\hat{A}$ is given by

$$\int_0^{L_x} dx \int_0^{L_y} dy \int_0^{L_z} dz\, \psi^*(x, y, z)\hat{A}\psi(x, y, z). \tag{32}$$

Note that whenever an integrand can be factorized into a product, then we can perform each integral independently, for example

$$\int_0^{L_x} dx \int_0^{L_y} dy \int_0^{L_z} dz\, f(x)g(y)h(z) = \left[\int_0^{L_x} dx\, f(x)\right] \times \left[\int_0^{L_y} dy\, g(y)\right] \times \left[\int_0^{L_z} dz\, h(z)\right]. \tag{33}$$

For example, say we want to compute the average value of $r^2 = x^2 + y^2 + z^2$ for the state $\psi_{2,1,1}(x, y, z) = \psi_2(x)\psi_1(y)\psi_1(z)$. First we can split the 3-dimensional integral into three pieces

$$\langle x^2 + y^2 + z^2\rangle = \langle x^2\rangle + \langle y^2\rangle + \langle z^2\rangle. \tag{34}$$

Next, we use the fact that the wave function is factorized and orthonormality of the wave functions to simplify these expressions. For example,

$$\begin{aligned}
\langle x^2\rangle &= \int_0^{L_x} dx \int_0^{L_y} dy \int_0^{L_z} dz\, \psi^*_{2,1,1}(x, y, z)x^2\psi_{2,1,1}(x, y, z) \\
&= \left[\int_0^{L_x} dx\, \psi^*_2(x)x^2\psi_2(x)\right] \times \underbrace{\left[\int_0^{L_y} dy\, |\psi_1(y)|^2\right]}_{=1} \times \underbrace{\left[\int_0^{L_z} dz\, |\psi_1(z)|^2\right]}_{=1} \\
&= \int_0^{L_x} dx\, \psi^*_2(x)x^2\psi_2(x).
\end{aligned} \tag{35}$$

Repeating the same derivation for the y^2 and z^2 integrals we arrive at the simple result

$$\langle x^2+y^2+z^2\rangle = \int_0^{L_x} dx\, \psi^*_2(x)x^2\psi_2(x) + \int_0^{L_y} dy\, \psi^*_1(y)y^2\psi_1(y) + \int_0^{L_z} dz\, \psi^*_1(z)z^2\psi_1(z). \tag{36}$$

This shows that the average of $x^2 + y^2 + z^2$ for the particle in a 3D box is just the sum of the individual averages for each degree of freedom.